FORM PTO-1390 U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371	ATTORNEY'S DOCKET NUMBER: BO 41866
	U.S. APPLN. NO. (If known, see 37 CFR 1.5) 09/807025

INTERNATIONAL APPLICATION NO.: PCT/NL99/00624	INTERNATIONAL FILING DATE: 8 OCTOBER 1999	PRIORITY DATE CLAIMED: 8 OCTOBER 1998

TITLE OF INVENTION: METHOD FOR COATING A SUPPORT PLATE AND FUEL CELL PROVIDED WITH SUCH A SUPPORT PLATE

APPLICANT(S) FOR DO/EO/US: Robert Christiaan MAKKUS, Edward BULLOCK, Arnoldus Hermanus Henderikus JANSSEN, Michel CASSIR

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. [X] This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. [ ] This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. [X] This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. [X] A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. [X] A copy of the International Application as filed (35 U.S.C. 371(c)(2))
   a. [X] is transmitted herewith (required only if not transmitted by the International Bureau).
   b. [X] has been transmitted by the International Bureau. (see attached copy of PCT/IB/308)
   c. [ ] is not required, as the application was filed in the United States Receiving Office (RO/US).
6. [ ] A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. [ ] Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)).
   a. [ ] are transmitted herewith (required only if not transmitted by the International Bureau).
   b. [ ] have been transmitted by the International Bureau.
   c. [ ] have not been made; however, the time limit for making such amendments has NOT expired.
   d. [ ] have not been made and will not be made.
8. [ ] A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. [ ] An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. [ ] A translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Item 11. to 16. below concern document(s) or information included:

11. [X] An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. [ ] An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. [X] A **FIRST** preliminary amendment.
    [ ] A **SECOND** or **SUBSEQUENT** preliminary amendment.
14. [ ] A substitute specification.
15. [ ] A change of power of attorney and/or address letter.
16. [X] Other items or information:

International Search Report
PCT/IPEA/409
PCT/IB/308
Abstract of the Disclosure on a Separate Sheet
Application Data Sheet

U.S. APPLICATION NO. (If known, see 37 CFR 1.5)	INTERNATIONAL APPLICATION NO.	ATTORNEY'S DOCKET NO.
09/807025	PCT/NL99/00624	BO 41866

	CALCULATIONS PTO USE ONLY
17. [X] The following fees are submitted:	
BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5)):	
Neither international preliminary examination fee (37 CFR1.482) nor international search fee (37 CFR1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO ..... $ 1,000.00	
International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO ..... $ 860.00	
International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO ..... $ 710.00	
International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) ..... $ 690.00	
International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) ..... $ 100.00	
ENTER APPROPRIATE BASIC FEE AMOUNT =	$ 860.00
Surcharge of $130.00 for furnishing the oath or declaration later than 30 months from the earliest claimed priority date (37 CFR 1.492(e)).	$ 130.00

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	
Total claims	9 - 20 =	0	X $18.00	$
Independent claims	2 - 3 =	0	X $80.00	$
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ $270.00	$

TOTAL OF ABOVE CALCULATIONS =	$ 990.00
Reduction of ½ for filing by small entity, if applicable. Applicant claims Small Entity Status under 37 CFR 1.27. +	$
SUBTOTAL =	$ 990.00
Processing fee of $130 for furnishing the English translation later than months from the earliest claimed priority date (37 CFR1.49(f)).	$
TOTAL NATIONAL FEE =	$ 990.00
Fee for recording the enclosed assignment (37 CFR1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). $40.00 per property+	$
TOTAL FEES ENCLOSED =	$ 990.00
	Amount to be refunded:
	charged:

a. [X] A check in the amount of $ **990.00** to cover the above fees is enclosed.

b. [ ] Please charge my Deposit Account No. **25-0120** in the amount of $ to cover the above fees. A duplicate copy of this sheet is enclosed.

c. [X] The Commissioner is hereby authorized to charge any additional fees which may be required by 37 CFR 1.16 and 1.17, or credit any overpayment to Deposit Account No. **25-0120**. A duplicate copy of this sheet is enclosed.

SEND ALL CORRESPONDENCE TO:

Customer No. 000466
YOUNG & THOMPSON
745 South 23rd Street
2nd Floor
Arlington, VA 22202
(703) 521-2297 facsimile (703) 685-0573

April 9, 2001

By _____
Roland E. Long, Jr.
Attorney for Applicants
Registration No. 41,949

PATENTS

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of

Robert Christiaan MAKKUS et al.

Serial No. (unknown)

Filed herewith

METHOD FOR COATING A SUPPORT PLATE AND FUEL CELL PROVIDED WITH SUCH A SUPPORT PLATE

PRELIMINARY AMENDMENT

Commissioner for Patents

Washington, D.C. 20231

Sir:

Prior to the first Official Action and calculation of the filing fee, please amend the above-identified application as follows:

IN THE CLAIMS:

Cancel claims 1-9.

Add the following new claims:

--10.(new) Method for coating a non-oxidised stainless steel support plate with an electrically conducting corrosion-resistant coating, comprising applying a diffusion barrier layer containing a titanium compound, followed by applying a nickel layer, characterised in that applying said diffusion barrier layer comprises the application of a titanium oxide containing compound before applying said nickel layer.

--11.(new) Method according to Claim 10, wherein at least one of said applied layers has a thickness of at least 25 µm.

--12.(new) Method according to claim 10, wherein an adhesion layer is applied to the support plate before titanium oxide is applied.

--13.(new) Method according to claim 12, wherein said adhesion layer comprises NiCrAlY.

--14.(new) Method according to claim 10, wherein at least one of said layers is applied by high velocity oxygen flame spraying.

--15.(new) Fuel stack comprising a number of cells each having a cathode, anode and electrolyte, wherein said cells are separated by a separator plate, said separator plate comprising a support plate of stainless steel coated on the anode side with a diffusion barrier layer comprising titanium oxide provided with a nickel layer, said diffusion layer comprising titanium oxide being provided before the application of said nickel layer.

--16.(new) Fuel cell according to Claim 15, wherein said titanium oxide layer and/or nickel layer has a thickness of at least 25 µm.

--17.(new) Fuel cell according to claim 15, wherein an adhesion layer is applied between said stainless steel support plate and said titanium oxide layer.

--18.(new) Fuel cell according to Claim 17, wherein said adhesion layer comprises NiCrAlY.

R E M A R K S

Following entry of this amendment, the claims now in the case are claims 10-18.

Respectfully submitted,

YOUNG & THOMPSON

By _____

Roland E. Long, Jr.
Attorney for Applicants
Customer No. 000466
Registration No. 41,949
745 South 23rd Street
Arlington, VA 22202
Telephone: 703/521-2297

April 9, 2001

Method for coating a support plate
and fuel cell provided with such a support plate

The present invention relates to a method for coating a non-oxidised stainless steel support plate with an electrically conducting corrosion-resistant coating, comprising applying a diffusion barrier layer containing a titanium compound, followed by applying a nickel layer. A method of this type is disclosed in German Offenlegungsschrift 19523637. High demands are imposed on that part of the fuel cell which is located on the anode side. On the one hand this must be capable of discharging the stream supplied via the gas distribution device on the anode side. On the other hand this must be sufficiently corrosion-resistant to meet current requirements in respect of service life. Currently a service life of a few ten thousand hours is required. Because of the aggressive environment resulting from carbonate material, high temperature and the relatively low potential at the anode, this side of the separator plate is particularly severely stressed.

In order to avoid the corrosion problems it is proposed in the abovementioned German Offenlegungsschrift to apply a coating, consisting of a titanium nitride layer on top of which a nickel layer has been applied, on the anode side of the stainless steel separator plate. This nickel layer provides protection but the base material from the stainless steel must be prevented from diffusing into the nickel. After all, it has been observed that the strength of the residual nickel layer decreases appreciably as a result of such a diffusion process and within 10 000 hours the residual nickel layer detaches from the stainless steel layer and the cell rapidly becomes inoperative. According to German Offenlegungsschrift 19523637, the thickness of the titanium nitride layer is preferably between 0.5 and 5 μm. It is assumed that the titanium nitride is converted to titanium oxide by contact with the carbonate material. However, it has been found that this oxide has a larger volume and consequently locally pushes away the nickel layer. Moreover, it has been found that a titanium oxide layer obtained in this way is not impermeable and attack on the base material can consequently not be prevented.

In German Offenlegungsschrift 4030943 an anode made up of porous nickel and titanium oxide is described. On contact with lithium carbonate lithium titanate is produced, which promotes moistening of the porous nickel anode because carbonate material penetrates into the anode more easily. The separator plate or bipolar plate is nickel-coated and consists of stainless steel material.

The aim of the present invention is to provide a method for coating a separator plate of a fuel cell wherein a diffusion barrier layer is used which remains intact even after prolonged operation and wherein the corrosion-resistant nickel layer arranged thereon is not affected.

This aim is achieved with a method as described above in that said titanium compound comprises titanium oxide.

As a result of applying titanium oxide directly to the stainless steel base material, no harmful reaction takes place when carbonate diffuses through the porous nickel top layer. It is assumed that TiO_2 in contact with the carbonate converts the top layer into Li_2TiO_3. This does not have any adverse effect on the electrical properties of the coating. The bulk of the TiO_2 is converted into a sodium-titanium bronze or a potassium-titanium bronze. This material still has barrier properties relative to the alloy elements from the stainless steel. A further guarantee that the barrier layer remains intact even during a prolonged period is achieved by giving the layer an appreciable thickness. Preferably the thickness is at least 25 μm and more particularly is between 40 and 50 μm.

The titanium oxide layer described above can be applied in any way known from the prior art. Examples are application of a plasma spray under atmospheric pressure or high velocity oxygen flame spraying, sputtering, vaporisation using an arc, adhesion and sputtering using an arc, ion plating or CVD.

According to a further advantageous embodiment of the invention the titanium oxide is applied to the stainless steel support only after an adhesion layer, such as a layer of NiCrAlY, has been placed thereon.

As described above, the invention is used in particular for a fuel cell in which the separator plate or bipolar plate on the anode side has been treated as described above. It must be understood that the method described above can be used in other applications under aggressive conditions where electrical conduction is required.

The invention will be explained below with reference to an illustrative embodiment shown in the drawing, in which the various components are not shown on the same scale. In the drawing:

Fig. 1 shows, diagrammatically in cross-section, part of an MCFC cell close to the separator plate according to the invention; and

Fig. 2 shows, in detail in cross-section, part of a separator plate facing the anode.

Fig. 1 shows part of an MCFC cell provided with a separator plate 7 which is adjoined

by a gas distribution device 4 on the anode side, with which current collector 8 is in contact, which is adjoined by an anode 5. Both the anode and the corrugation can be made of nickel material. The anode consists more particularly of nickel containing 10 % (by wt.) Cr.

The separator plate 7 is shown in detail in Fig. 2. This separator plate consists of a support of stainless steel material, such as 3 AISI 310 having a thickness of, for example, 0.5 mm. An adhesion layer 6 composed of a metal chromium aluminium yttrium alloy, such as NiCrAlY, is applied on top of this. The thickness of this layer is approximately 40-60 μm. The adhesion layer material can be applied in powder form by using as the starting material an NiCrAlY powder having a particle size of between 10 and 45 μm, which is applied using the HVOF spraying technique.

An adhesion layer of this type is applied in order to compensate for the difference in the coefficient of expansion between stainless steel and the titanium oxide layer. Before applying such an adhesion layer to the stainless steel support material, the stainless steel material can be roughened by any method known from the prior art. For example roughening takes place by means of grit blasting with fine Al_2O_3 grit.

A titanium oxide layer having a thickness of between 40 and 50 μm is then applied thereon using the high velocity oxygen flame spraying technique. This layer is indicated by 2. The starting material used for this layer is a powder having a particle size of between 5 and 20 μm. This powder can optionally be doped with a pentavalent ion, in particular with niobium or tantalum. Niobium is the most preferred. The porosity of the titanium oxide layer is typically 2 %. A nickel layer 3, having a thickness which is likewise between 25 and 50 μm, is applied on top of said titanium oxide layer by any method known from the prior art. In this case also the HVOF spraying technique is preferably used.

In tests under corrosive conditions with the potential applied to the anode, as is to be expected in use, no substantial attack on the stainless steel base material was detected at a temperature of approximately 650 °C after 3 000 hours. On the basis of this it can be extrapolated that a service life of more than 40 000 hours is achievable.

Although the invention has been described above with reference to a preferred embodiment, it must be understood that modifications can be made thereto which are immediately obvious to those skilled in the art after reading the above description and are within the scope of the appended claims.

Claims

1. Method for coating a non-oxidised stainless steel support plate with an electrically conducting corrosion-resistant coating, comprising applying a diffusion barrier layer containing a titanium compound, followed by applying a nickel layer, characterised in that said titanium compound comprises titanium oxide.

2. Method according to Claim 1, wherein at least one of said applied layers has a thickness of at least 25 μm.

3. Method according to one of the preceding claims, wherein an adhesion layer is applied to the support plate before titanium oxide is applied.

4. Method according to Claim 3, wherein said adhesion layer comprises NiCrAlY.

5. Method according to one of the preceding claims, wherein at least one of said layers is applied by high velocity oxygen flame spraying.

6. Fuel cell stack comprising a number of cells each having a cathode, anode and electrolyte, wherein said cells are separated by a separator plate, said separator plate comprising a support plate of stainless steel coated on the anode side with a diffusion barrier layer comprising titanium oxide provided with a nickel layer.

7. Fuel cell according to Claim 6, wherein said titanium oxide layer and/or nickel layer has a thickness of at least 25 μm.

8. Fuel cell according to Claim 6 or 7, wherein an adhesion layer is applied between said stainless steel support plate and said titanium oxide layer.

9. Fuel cell according to Claim 8, wherein said adhesion layer comprises NiCrAlY.

ABSTRACT OF THE DISCLOSURE

Method for coating a non-oxidised stainless steel support plate and a MCFC fuel cell stack provided with a separator plate coated in this way. First a diffusion barrier layer and then a nickel layer are applied to the anode side of said support plate. Said diffusion barrier layer consists of titanium oxide and the adhesion between titanium oxide and the support plate can be improved by providing an adhesion layer.

Fig 1

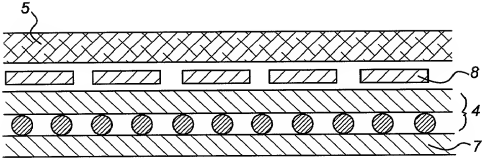


Fig 2

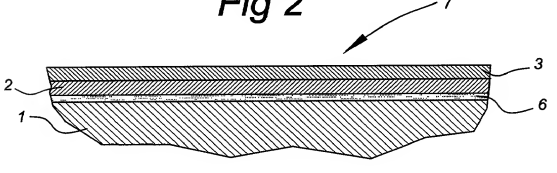
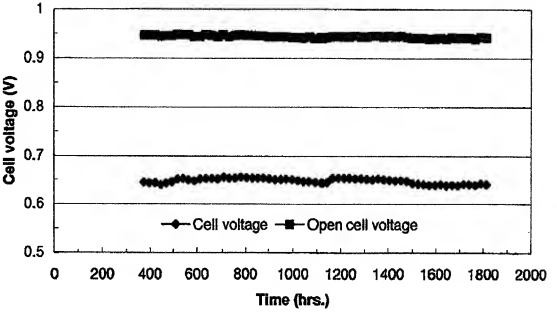


Fig 3



COMBINED DECLARATION AND POWER OF ATTORNEY

(ORIGINAL DESIGN, NATIONAL STAGE OF PCT OR CIP APPLICATION)

'As a below named inventor, I hereby declare that

My residence, post office address and citizenship are as stated below next to my name, I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

Method for coating a support plate and fuel cell provided with such a support plate

the specification of which: (complete (a), (b) or (c) for type of application)

REGULAR OR DESIGN APPLICATION

a. [ ] is attached hereto.

b. [ ] was filed on as Application
Serial No. and was amended on
(if applicable)

PCT FILED APPLICATION ENTERING NATIONAL STAGE

c. [x] was described and claimed in International application No. PCT/NL99/00624
filed on 8 October 1999
and as amended on (if any)

ACKNOWLEDGEMENT OF REVIEW OF PAPERS AND DUTY OF CANDOR

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, paragraph 1.56(a).

In compliance with this duty there is attached an information disclosure statement 37 CFR 1.97

PRIORITY CLAIM

I hereby claim foreign priority benefits under Title 35. United States Code paragraph 119 of any foreign application (s) for patent of inventor's certificate listed below and have also identified below any foreign application for patent of inventor's certificate having a filing date before that of the application on which priority is claimed.

(complete (d) or (e))

d. [ ] no such applications have been filed

e. [X] such applications have been filed as follows

EARLIEST FOREIGN APPLICATION(S), IF ANY FILED WITHIN 12 MONTHS (6 MONTHS FOR DESIGN) PRIOR TO SAID APPLICATION

Country	Application Number	Date of filing (day, month, year)	Date of Issue (day, month, year)	Priority claimed
The Netherlands	1010269	8 October 1998		Yes

ALL FOREIGN APPLICATION(S), IF ANY FILED MORE THAN 12 MONTHS (6 MONTHS FOR DESIGN) PRIOR TO SAID APPLICATION

CONTINUATION-IN-PART

(Complete this part only if this is a continuation-in-part application)

I hereby declare claim the benefit under Title 35, United States code, paragraph 120 of any United States application(s) listed below and, insofar as the subject matter of each of the claim of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, paragraph 112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, paragraph 1.56(a) which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

(Application Serial No.) (Filing date) (Status) (patented, pending, abandoned)

(Application Serial No.) (Filing date) (Status) (patented, pending, abandoned)

POWER OF ATTORNEY

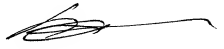
As a named inventor, I hereby appoint the following attorney(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith: Robert J. PATCH, Reg. No. 17,355, Andrew J. PATCH, Reg. No. 32,925, Robert F. HARGEST, Reg. No. 25,590, Benoît CASTEL, Reg. No. 35,041, Eric Jensen, Reg. No. 37,855, and Thomas W. PERKINS, Reg. No. 33,027 and Roland E. Long, Jr. Reg. No. 41,949 c/o YOUNG & THOMPSON, Second Floor, 745 South 23rd Street, Arlington, Virginia 22202.

Address all telephone calls to Young & Thompson at 703/521-2297.

Customer No. 000136

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that wilful false statements and the like so made are punishable by fine or imprisonment, or both under Section 1001 of Title 18 of the United States Code and that such wilful false statements may jeopardize the validity of the application or any patent issued thereon.

1 - 00 Full name of sole or first inventor: **MAKKUS, Robert Christiaan**
Inventor's signature



Date May 23 2001 Country of Citizenship: The Netherlands
Residence: ALKMAAR, The Netherlands NLX
Post Office Address: Karekietstraat 8, NL-1826 JM ALKMAAR, The Netherlands

2 - 00 Full name of second inventor: **BULLOCK, Edward**
Inventor's signature

Date May 23 2001 Country of Citizenship: Great Britain
Residence: BERGEN, The Netherlands NLX
Post Office Address: Eikenlaan 16, NL-1861 GV BERGEN, The Netherlands

3 - 00 Full name of third inventor: **JANSSEN, Arnoldus Hermannus Henderikus**
Inventor's signature

Date May 23 2001 Country of Citizenship: The Netherlands
Residence: ALKMAAR, The Netherlands NLX
Post Office Address: G.A. Holzmüller-Teengsstraat 3, NL-1827 PJ ALKMAAR, The Netherlands

4 - 00 Full name of fourth inventor: **CASSIR, Michel**
Inventor's signature

Date May 23 2001 Country of Citizenship: France
Residence: PARIS, France FRX
Post Office Address: 4, rue Edmond Gondinet, F-75013 PARIS, France
CHECK PROPER BOX(ES) FOR ANY ADDED PAGE(S) FORMING A PART OF THIS DECLARATION